Spectrophotometric determination of deltamethrine in pure and environmental samples

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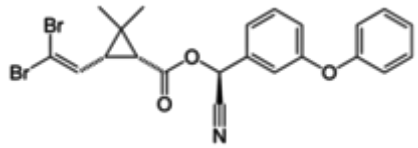
Abstract . An accurate and sensitive spectrophotometric method has been developed for the determination of deltamethrine (DLM) [(S)-Cyano-(3-phenoxyphenyl)-methyl] 3-(2, 2-dibromoethenyl)-2, 2-dimethyl-cyclopropane-1-carboxylate by reduction of 2, 3, 5-triphenyltetrazolium (TET) by cyanide ion yield from methanolic alkaline hydrolysis of DLM and subsequent react with p-nitrobenzyldehyde to form a good reduction agent for TET to yield the formazan has maximum absorption at 483 nm. Maximum colour absorption was attained in 15 min in the presence of 0.5 N NaOH. In addition to the considerably high values of the molar absorptivity of the chromogen formed, ideal adherence of the colour absorption to the Beer-Lambert law permitted a sensitive micro and nano determination of DLM in both pure and environmental samples. The Beer's law was obeyed over the concentration range of (0.1-3) µg mL^{-1}. The analytical parameters were evaluated in the proposed method and have been successfully applied for the determination of DLM in its formulations and environmental samples. The aim of this study is it to develop rapid sensitive analytical method to evaluate the micrograms of DLM in various samples.

Key word: deltamethrine, spectrophotometric determination, tetrazolium, cyanide ion

1. Introduction

Pyrethroid pesticides are toxic to man and animals, carcinogenic to human and exert genotoxic, mutagenic and embryo toxic effects. The use of Pyrethroid insecticides is increasing for agriculture, commercial pest control [1]. The concern for human and animal food has become very important lately, especially after the huge population explosion, there is an urgent need to increase food resources and improve their quality. This is not successful with the presence of agricultural pests. The use of agricultural pesticides has spread to eliminate agricultural pests, the increase in these pesticides negatively affects the health of living organisms, especially human, and so there must be a balance between the abundant productivity and the process of consumption of pesticides. Several studies have shown that the residues of pesticides in the soil is a key factor for food contamination and biological chains **[2].** DLM destroy insects on contact and through digestion. The Delta destroys insects by paralyzing its nervous system. It has a wide range in eliminating insect caterpillars that infect apples, pears, and for the control of bugs, crustaceans and white flies that infect vegetables in greenhouses and tomatoes as well as ornamental plants [3]. Several technique found to estimate various types of pesticide spatially with high performance liquid chromatography [4-7],Mass spectrophotometric [9],

GC-MASS technique[10-11] Spectrophotometric studied still the simpler, cheap and favourable technique to evaluate pesticide and There are many studies conducted using this technique[12-13]



Scheme1. The chemical structure of the deltamethrine

2. Experimental

2.1. Apparatus

Absorption measurements were made by spectrophotometer Shimadzu (UV-160A) in 1cm optical quartz

2.2. Chemicals

Chemical reagents used were of analytical grade. DLM (provided from Ministry of Agriculture \Plant Protection Department \ National Centre for Pesticide Control)

Solution (100ppm) was prepared by dissolving 0.05 g with methanol and diluted to 500 ml in calibrated flask then stored in amber coloured bottle and kept in refrigerator. The solution were diluted as needed. P- nitrobenzaldehyde (0.066M) was prepared by dissolving 1g with 100 ml methanol. Tetrazolium (1.97×10^{-4}M) was attended by dissolving ٠.0066g in 10 mLof methanol and diluted to the mark in a 100 volumetric flask with the same solvent. Sodium hydroxide (0.5M) was prepared by dissolving 2 g of sodium hydroxide in methanol and diluted to 100 ml in calibrated flask.

2.3. Recommended procedures

Different aliquots (0.05-1.6) mL equivalents to (0.1-3) ppm for DLM (100 μg mL^{-1}) was transferred into a series of calibrated flasks by means of a micro burette and the total volume was adjusted to 5.0 mL. To each flask, 0.3 mL of 0.5 M NaOH was treated to hydrolysed and release cyanide ion, the flasks were stoppered and the contents were mixed for 5 min then 1 mL of para nitrobenzaldehyde was added. Finally one mL tetrazolium was added and mixed well, the volume was diluted to the mark with methanol. The colour intensity of reduced tetrazolium was measured after 15.0 min against reagent blank solution treated similarly at their corresponding λmax 481nm.

2.4. Procedure for formulations

1- Solid formulation (raid)

Weight 0.5 g (0.05g\100 g) dissolved with 10 ml methanol and separate the insoluble mater by filter paper then complete the solution to the mark with same solvent to prepare 10μ g DLM and complete the procedure.

2- Solution formulation

A volume of 1 mLof deltamethrine formulation (2.5 g\100 mL), equivalent to 25mg of DLM placed in volumetric flask of 25ml with methanol to prepper stock solution of 1000 μg. The DLM was determined by the aforesaid procedures by taken a proper dilution from the stock solution.

2.5. Procedure for water sample

Applied the suggested procedure on determination of DLM in water sample done with 20 mL of tap water. To avoid the interferences from other ions in the sample, 1 mL of EDTA (0.1g\25 mL in methanol) was added to mask various metal ions. The sample spiked with 1 mL of 1000 ppm DLM then complete the volume to the mark with water. With 35 mL of ethyl acetate (7 time x 5 mL) extract DLM was done then evaporate the solvent on water bath at 50°C. , The residue was dissolved in 10 mL methanol then the volume of the extract was made up to the mark with methanol in 25mL calibrated flask. The solution was analysed as described above**.**

2.6. Procedure for soil sample

A known weight of 2.5 g well-powdered soil sample spiked with 1 mL of 1000ppm deltamethrine mixed and stirring well. The deltamethrine extract with 25 mL (5 time 5mL) methanol then filtered using Whitman filter paper and made up to 25mL with the same solvent.

3.Result and Discussion

3.1 Spectral characteristic

The method involved methanolic basic hydrolysis of DLM to release free cyanide. The cyanide anion react with p-nitrobenzyldehyed in alcoholic sodium hydroxide to form cyanohydrin which reduce the tetrazolium to yield pale orange colour formazan having λmax at480 nm. The reagent blank has practically no absorbance at 480 nm as shown in Figure 1. The formation of coloured formazan with the reagents was shown in Scheme 2.

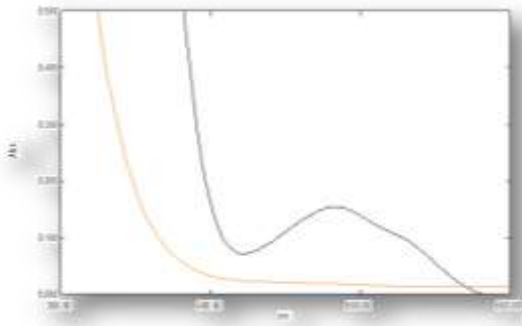
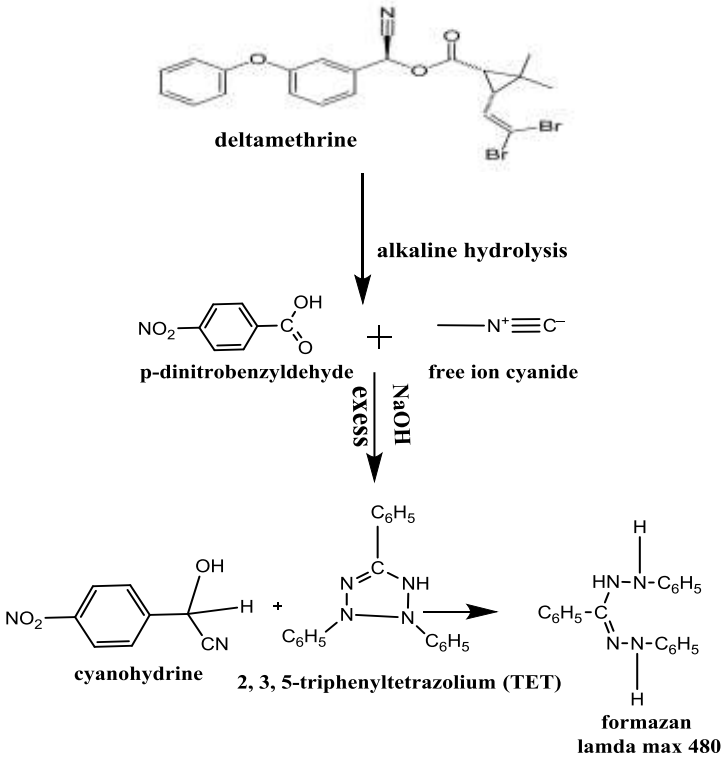


Figure (1) absorption spectra of reduced TETR with 2µ g of DLM



Scheme (2) reduction bath way of tetrazolium by cyanide ion

3.2. Optimization study

Hydrolysis of DLM to release free cyanide was studied at different alkalinity. It was showed that alkaline conditions must require for the complete hydrolysis. Maximum hydrolysis was observed with 0.3 mL sodium hydroxide at 5 min. However, the following optimum concentrations and volume ranges were needed for colour development. In the proposed methods, it was found that 1.0 mL of 1.0 % (w/v) p- nitrobenzyldehyde was suitable for colour development to achieve the maximum intensity after 15 min (Figure2) and what is worth to mention the study done at dark condition.

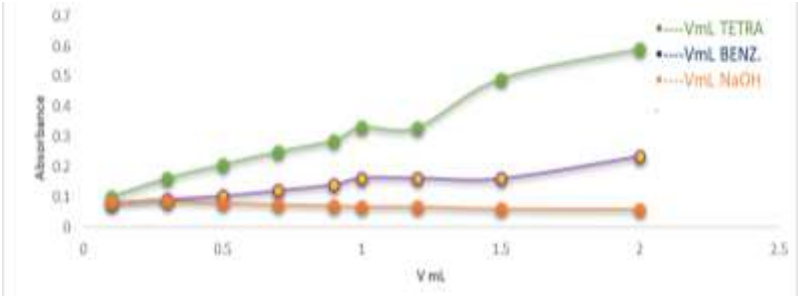


Figure (2) effect of volume of NaOH (2%), volume of TET. (0.0066%) and volume of BENZ. (1%)

3.3. Effect of foreign species

Study the interference effect from foreign ions commonly found with DLM were studied by adding known amounts of diverse ions to standard solution contained ٢.0 µg DLM and 1 ml of (0.1 g in 25 ml) EDTA in ٥ mL of final solution then analysed by the proposed method.The results shows that the excipients don't interfere in the determination of DLM in tolerance limit less than 10 ppm (Table 1).

Table 1. Effect of foreign species for determination of deltamethrine (2.0 µg per 5 mL)

Cationic species 10 µg mL^{-1}	Relative error %
Na^{+1}	**-1.500**
Ca^{+2}	**1.500**
Ba^{+2}	**0.000**
NO_3^{-1}	**-2.500**
SO_4^{-2}	**-3.000**
Cl^{-1}	**1.500**
CO_3^{-2}	**-1.500**

3.4 Calibration curves and analytical data

Employing the best condition, the absorbance of formazan at 483nm versus different standard concentration of DLM was done. The linearity of the obtained plot of the DLM was in the concentration range (0.1-3) µg.mL^{-1} as shown in Figure (3) .The statistical treatment of the analytical data are summarized in Table (2).

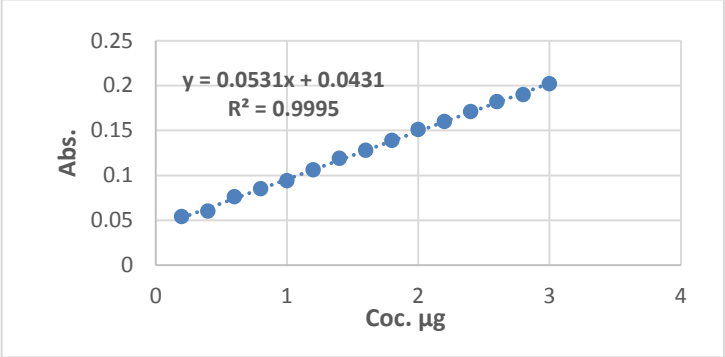


Figure 3. Regration equation of proposed method

Table 2. Optical characteristics and statistical data

Parameter	Value
λmax (nm)	482
concentration (µg mL $^{-1}$)	0.2-3
Molar absorptivity L. mol $^{-1}$ cm $^{-1}$)	26563
Sandle sensitivity	0.01903
Regration equation	0.0526x+0.0442
slop	0.0526
Correlation Coefficient (r)	0.9993
Relative Standard Deviation (RSD %)	0.0016
Detection limit µg mL^{-1} *	0.040
Limit value µg mL^{-1} *	0.400
colour	Pale orang

*LOQ = 10s / b
* LOD = 3.3s / b

3.5. Applications

The method apply to determination DLM in formulations (Table 3), soil, water samples and recovery of standard addition method (Table4)

Table 3. Determination of insecticide DLM in its formulations.

Formulation	µg	Recovery% ±SD	Reference method(3)
Raid (0.05g %) (Jorden) Delta baz25 Ec (2.5g%)(Jorden)	0.8	93.7 ±0.020	**96.4 ±0.8**
	1.6	93.7 ±0.025	
	1.2	97.9 ±0.080	
	0.8	97.5±0.025	
	1.6	96.06±0.020	
	1.2	95.8±0.01	

Table 4. Recovery of deltamethrine from soil and water samples

sample	Added amount µg	Found amount µg	Recovery±SD
Tap water	0.4	0.39	97.50±0.0350
	0.8	0.73	91.25±0.0040
	1.2	1.15	95.00±0.0050
soil	0.4	0.4	100.0±0.0045
	0.8	0.8	100.0±0.0055
	1.2	1.17	97.50±0.0074

3.5.1 Standard addition

Standard addition method was applied to evaluate DLM in presence of different specious to increase the insurance, the proposed spectrophotometric method was applied (weight 1 g from each : glucose , starch , acacia , magnesium setrate and lactose) mixed well and weight 0.01 g from the mixture dissolved in methanol and complete the volume to the mark with distilled water to ٢5mLvolumetric flask). Following the standard addition technique. Good recovery(R 107%±S.D) of the drug present in studied sample indicates that no interference from the matrix affect the determination of DLM. Figure (10) shows the standard additions plot and Table (10) shows the result of recovery for the method.

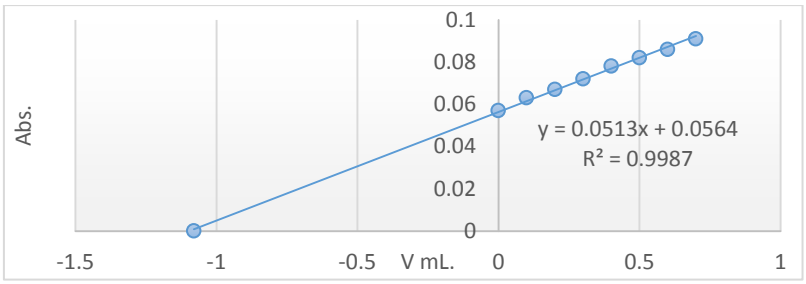


Figure 4. Standard addition plot applied to determination of 0.4µg of DLM

3.5.2.Accuracy and precision The precision and accuracy of the proposed method was tested by analysing five replicate samples of DLM in three different levels (within Beer's law range). The result listed in Table (5) indicates an acceptable accuracy and precision to suggested work.

Table 5. Evaluation of precision and accuracy

Taken(µg\ml)*	Recovery	precision	Accuracy
	%	(RSD %)	R.E%
1	98	2.3×10^{-2}	-3
2	98	3.5×10^{-2}	-1
3	96	3×10^{-2}	-4.3

*Five replicate

CONCLUSION

The proposed method was found to be very simple, rapid, low cost and fairly selective than other method. The proposed method was applied to the analysis of DLM in pure, and can be used for the routine analysis of commercial formulations. The release of free cyanide ion from DLM and reaction with P- nitro benzaldehyde makes it possible for reduction TET in alkaline media then formation of formazan to give a light orange colour. The accuracy and precision of the proposed method were tested by analysing five replicate of DLM for three different concentrations, the values of RSD% and relative error Erel. % indicated good accuracy and precision.

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